

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 65/10, 65/20	A1	(11) International Publication Number: WO 96/13540
		(43) International Publication Date: 9 May 1996 (09.05.96)
<p>(21) International Application Number: PCT/US95/13701</p> <p>(22) International Filing Date: 24 October 1995 (24.10.95)</p> <p>(30) Priority Data: 08/331,305 28 October 1994 (28.10.94) US</p> <p>(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(72) Inventor: DRYSDALE, Neville, Everton; 227 Welsh Tract Road, Newark, DE 19702-1026 (US).</p> <p>(74) Agents: SCHAEFFER, Andrew, L. et al.; E.I. Du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: AL, AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: POLYMERIZATION OF CYCLIC ETHERS USING SELECTED METAL COMPOUND CATALYSTS</p> <p>(57) Abstract</p> <p>A process for polymerizing oxiranes, oxetanes, oxepanes, dioxolanes, trioxanes, and tetrahydrofurans to their respective polymers by contacting them with a selected metal compound and an accelerator which is a selected vinyl ester or a selected phosphorous compounds.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

TITLEPOLYMERIZATION OF CYCLIC ETHERS
USING SELECTED METAL COMPOUND CATALYSTSFIELD OF THE INVENTION

5 This invention concerns the polymerization of
oxiranes, oxetanes, oxepanes, 1,3-dioxolanes,
1,3,5-trioranes, and tetrahydrofurans to linear
polyethers catalyzed by selected metal compounds
together with selected accelerators.

10 BACKGROUND OF THE INVENTION

Cyclic ethers are polymerized by various means to
give products of widespread utility. For instance,
ethylene oxide is polymerized to polyethylene oxide
which is useful, in lower molecular weight grades, for
15 ceramics (as a binder), cosmetics, lubricants,
polyurethanes; and in higher molecular weight grades,
for packaging film, denture adhesives, lubricants,
flocculation and for other articles and products.
Tetrahydrofuran (THF) is polymerized to poly(tetra-
20 methylene ether) glycol which is useful in the
preparation of Spandex fibers; polyurethane resins which
are useful in elastomeric parts; and thermoplastic
elastomers which are useful for molding various
mechanical parts. Therefore, improved methods of making
25 these polymers are sought.

U.S. Patent 3,842,019 describes the polymerization
of oxiranes and other small ring compounds by a presumed
cationic mechanism, using as the catalyst the
decomposition products of metal perfluoroalkyl-
30 sulfonates. These catalysts are described as "latent",
that is no reaction occurs until the metal salt is
decomposed. The reactions reported are relatively slow,
even at elevated temperatures.

U.S. Patents 5,084,586 and 5,124,417 describe the
35 cationic polymerization of various monomers, including

cyclic ethers, using onium cations, whose corresponding anions are fluororalkylsulfatometallates. Onium ion catalyzed cationic polymerizations are known, and there is no mention in these patents of the use of metal salts not containing onium ions, such as metal triflates, as catalysts for the polymerization of cyclic ethers.

J. S. Hrkach, et al., *Macromolecules*, vol. 23, p. 4042-4046 (1990) describe the polymerization of tetrahydrofuran using trimethylsilyl trifluoromethanesulfonate as the initiator. No mention is made of any other triflates as catalysts for this polymerization.

G. A. Olah, et al., *J. Appl. Polym. Sci.*, Vol. 45, 1355-1360 (1992) describe the use of boron, aluminum and gallium tris(triflate) to catalyze the polymerization of THF.

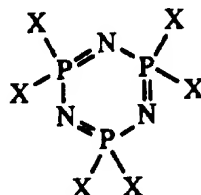
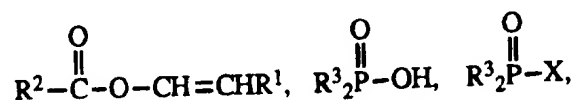
S. L. Borkowsky, et al., *Organometal.*, Vol. 10, p. 1268-1274 (1991) report that certain zirconium complexes can initiate the polymerization of tetrahydrofuran. No mention is made of zirconium perfluoroalkylsulfonates, or of copolymers.

I. Yamashita, et al., *Kogyo Kagaku Zasshi*, vol. 71, p. 1061-1064 (1968) describes the polymerization of tetrahydrofuran using a catalyst system consisting of a Lewis acid such as ferric chloride and a phosphorous compound such as triphenyl phosphite. The use of metal perfluoroalkylsulfonates is not mentioned.

SUMMARY OF THE INVENTION

This invention concerns a process for the polymerization of cyclic ethers, comprising, contacting one or more oxiranes, oxetanes, tetrahydrofurans, oxepanes, 1,3-dioxolanes or 1,3,5-trioxanes with a compound of the formula $MZ_3 \cdot Q_t$, and an accelerator which is a compound of the formula

3



wherein:

R^1 is hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^2 is hydrogen, hydrocarbyl or substituted hydrocarbyl;

5 each R^3 is independently hydrocarbyl or substituted hydrocarbyl;

each X is independently chlorine, bromine or iodine;

10 M is a metal selected from the group consisting of strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron,

15 cobalt, vanadium, niobium, tungsten, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, aluminum, gallium, indium, thulium, germanium, tin, lead, arsenic, antimony and bismuth;

at least one of Z is an anion of the formula $-SO_3R^5$, wherein R^5 is perfluoroalkyl containing 1 to 12

20 carbon atoms or part of a fluorinated polymer wherein the carbon atoms alpha and beta to the sulfonate group are together bonded to at least four fluorine atoms, or tetraphenylborate, and the remainder of Z is oxo or one or more monovalent

25 anions;

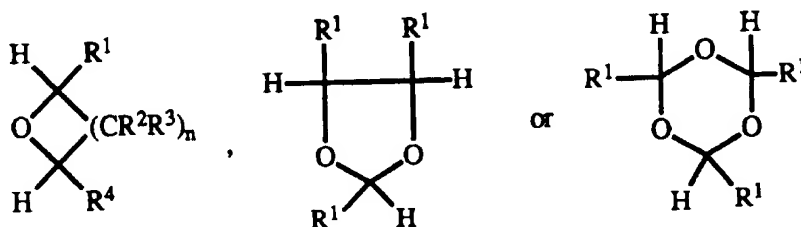
- s is 1 when M is silver;
s is 2 when M is strontium, barium, cobalt, rhodium,
iridium, palladium, platinum, chromium, zinc,
cadmium or mercury;
5 s is 3 when M is scandium, yttrium, a rare earth
metal, arsenic, antimony, bismuth, gold, iron,
ruthenium, osmium, aluminum, gallium, indium or
thulium;
s is 4 when M is titanium, zirconium, hafnium,
10 molybdenum, germanium, tin, or lead;
s is 5 when M is rhenium, vanadium, niobium or
tantalum;
s is 6 when M is tungsten;
Q is a neutral ligand;
15 t is 0 or an integer of 1 to 6; and
provided that each oxo group present counts as two of s.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

- In the polymerization process described herein one
or more cyclic ethers, oxiranes, oxetanes, 1,3-dioxo-
20 lanes, 1,3,5-trioxanes, or tetrahydrofurans are
polymerized to form a polyether. Oxirane (more commonly
called epoxide) is herein given its usual structure, a
saturated three membered ring containing two carbon
atoms and one oxygen atom. Oxetane is also given its
25 common meaning, a saturated four membered ring
containing three carbon atoms and one oxygen atom. The
term oxepane means a saturated seven membered ring
containing six carbon atoms and one oxygen atoms. The
term 1,3-dioxolane means a saturated five membered ring
30 which contains two oxygen atoms separated by 1 carbon
atom. The term 1,3,5-trioxane means a six membered ring
containing 3 oxygen atoms in which the oxygen atoms and
carbons atoms are alternated. All of these terms
35 are substituted with hydrocarbyl or hydrocarbylene

groups containing 1 to 20 carbon atoms. The hydrocarbylene groups may form carbocyclic rings, which include bicyclic, tricyclic, etc., systems. By a hydrocarbylene group herein is meant a divalent radical containing carbon and hydrogen which is part of a carbocyclic ring.

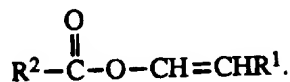
Preferred cyclic ethers have the formula



wherein n is 2 or 4 and each R^1 , R^2 , R^3 and R^4 is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms. Some of these cyclic ethers polymerize to give repeat units of the formula $-\text{CHR}^1(\text{CR}^2\text{R}^3)_n\text{CHR}^4\text{O}-$. In a more preferred cyclic ether all of R^1 , R^2 , R^3 and R^4 are hydrogen. In another more preferred cyclic ether where $n=2$, R^1 , one of R^2 , both of R^3 and R^4 are hydrogen, and the remaining R^2 is alkyl containing 1-4 carbon atoms, especially preferably the remaining R^2 is methyl. By hydrocarbyl herein is meant a univalent radical containing carbon and hydrogen.

The polymerization is run in the presence of an accelerator. Suitable accelerators include selected vinyl esters and selected phosphorous compounds.

The vinyl ester accelerators have the formula



In a preferred vinyl ester R^1 is hydrogen or alkyl, more preferably hydrogen or n -alkyl. In another preferred vinyl ester R^2 is alkyl, phenyl, or substituted phenyl, more preferably n -alkyl. In an

especially preferred vinyl ester R^1 is hydrogen and R^2 is methyl.

In the accelerators which are phosphorous compounds it is preferred if each R^3 is independently alkyl, phenyl, or substituted phenyl, more preferably n-alkyl containing 1, 2, 3 or 4 carbon atoms or phenyl. It is also preferred if X is chlorine.

By substituted hydrocarbyl (or substituted in substituted phenyl) is meant that the moiety may contain inert substituents (functional groups). By inert is meant that they don't react with any of the starting materials or products nor interfere with the polymerization. Such substituents include (linear) ether, alkyl, aryl, and halo.

An important consideration in the preparation of polyethers is the number average molecular weight (M_n) of the polyether and its molecular weight distribution. When the polyether is to be used as a monomer in the preparation of another polymer (usually in the diol form), it is often preferred that the M_n of the polyether be in the range of about 400 to about 20,000, preferably about 500 to about 5,000.

The catalyst may be yttrium or a rare earth compound of the formula MZ_3 where M is a trivalent ion of yttrium, or one of the rare earths, lanthanum, cerium, praeaseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

Preferred metals, M, are strontium, scandium yttrium, the rare earth metals, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, rhenium, iron, ruthenium, palladium, copper, gold, zinc, tin and bismuth. More preferred metals are yttrium, the rare earth metals, and scandium. Especially preferred metals are yttrium,

ytterbium, dysprosium, erbium, neodymium, lanthanum, and scandium. Another preferred metal is "mischmetall" (sometimes also called "didymium"), which is a mixture of rare earth metals as obtained from the ore.

5 It is currently believed monovalent anions that are relatively nonnucleophilic are useful as Z. Examples of such anions are tetraphenylborate, $^{-}\text{SO}_3\text{R}^5$, wherein R^5 is perfluoroalkyl, or wherein R^5 is part of a fluorinated polymer wherein the carbon atoms alpha and beta to a
10 sulfonate group are together bonded to at least 4 fluorine atoms (as in $^{-}\text{CF}_2\text{CF}_2\text{SO}_3^{-}$). It is preferred if R^5 is perfluoroalkyl. In a particularly preferred embodiment, R^5 is trifluoromethyl, and the anion is herein called "triflate".

15 Generally speaking, any metallic compound in which the correct metal in the correct oxidation state (see above) is present and bonded to a triflate or similar anion will be a catalyst. Such a compound must of course be reasonably stable during the polymerization or
20 decompose to another compound which is still a triflate (or similar anion) compound of the metal in the correct oxidation state. It has been found that, in general, the greater the number of triflate groups bonded to the metal cation, the more active the metal compound will be
25 as a catalyst. It is preferred if half or more of the anions (Z) bound to each metal cation is triflate or a similar anion.

The metal catalysts may optionally contain one or more neutral ligands coordinated to the metal. By a
30 neutral ligand is meant a neutral compound that can coordinate with the catalysts, usually the metal cation. Neutral ligands include water, and ethers such as dimethyl ether and tetrahydrofuran.

The metal catalysts may contain other anions than
35 triflate and similar anions, and tetrafluoroborate,

although at least one of triflate or tetrafluoroborate anions must be present. Some other useful anions are alkoxide, particularly lower alkoxide containing 1-4 carbon atoms, acetylacetonate, cyclopentadieneide, pentamethylcyclopentadieneide, t-butylacetylacetonate, and halide. It is preferred if all of the anions are triflate.

In general, the higher the molar ratio of metal compound to cyclic ether monomer originally present, the lower the molecular weight of the resulting polyether will be. Similarly, the higher the ratio of accelerator (if present) to monomer originally present, the lower the molecular weight of the polyether will be. It is currently believed that the effects of these two ratios are cumulative.

The polymerization may be run at a temperature of about -80°C to about 130°C. If this temperature is above the boiling point of the cyclic ether monomer, a pressure vessel may be used. A preferred temperature is ambient to the boiling point of the monomer, or 110°C, whichever is lower. An inert solvent such as di-n-butyl ether, diethyl ether or toluene may be used, but it is preferred if solvents are not present. Protic compounds such as water, methanol and ethanol should preferably not be present, and it is convenient to exclude them by drying the starting materials and keeping the process under an inert dry gas such as nitrogen. As in most chemical processes, the ingredients should be mixed at least initially. Continued agitation is preferred to assure that the process materials remain well mixed, and to avoid overheating. The polymerization is mildly exothermic. If the polymerization temperature goes up appreciably, refluxing of the monomer may be used to help cool the process.

The polymerization process can be performed in a variety of ways known to those skilled in the art. It can be done by batch, semi-batch and continuous processes. Continuous processes include continuous stirred tank reactor(s) with one or more stages, and/or plug flow reactors. Other variations will be evident to those skilled in this art.

In the polymerization process disclosed herein the catalyst may be recovered and reused. It may be recovered from the polymerization process by extracting the polymer formed with water. The recovered catalyst may be used again in the polymerization. The aqueous washings may be concentrated by removal of the water (as by evaporation) and the solid catalyst recovered.

15

EXAMPLES

In the following non-limiting Examples, the following abbreviations are used:

GPC - gel permeation chromatography
Mn - number average molecular weight
Mw - weight average molecular weight
PD - polydispersity, Mw/Mn
PS - polystyrene
RB - round-bottomed
STD - standard
THF - tetrahydrofuran

20

EXAMPLE 1

Polymerization of THF with Diethyl Chlorophosphite and Ytterbium Triflate

In a dry box, ytterbium triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphite (1.00 mL) were added. After 17 hours the polymerization was terminated via the addition of water,

35

THF and ether. The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum affording 12.63 g of polymer. GPC analysis (PS STD.): $M_n = 10200$, $M_w = 20100$, $PD = 1.96$.

5

EXAMPLE 2Polymerization of THF withDiphenylphosphinic Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (2.00 g) and diphenylphosphinic acid (1.00 g) were weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) was added. After 17 hours the polymerization was terminated via the addition of water, THF and ether. The resulting white mixture was filtered through Celite. The resulting filtrate was washed with water, concentrated at reduced pressure and dried under vacuum affording 8.22 g of polymer. GPC analysis (PS STD.): $M_n = 50900$, $M_w = 112000$, $PD = 2.21$.

15
20EXAMPLE 3Polymerization of THF withDiethyl Chlorophosphite and Erbium Triflate

In a dry box, erbium triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphite (2.00 mL) were added. After 17 hours the polymerization was terminated via the addition of water, THF and ether. The separated organic phase was again washed with water. The organic phase was concentrated at reduced pressure and then dried under vacuum affording 9.68 g of polymer. GPC analysis (PS STD.): $M_n = 10800$, $M_w = 19600$, $PD = 1.82$.

25
30

EXAMPLE 4Polymerization of THF withDiethyl Chlorophosphite and Neodymium Triflate

In a dry box, neodymium triflate (2.00 g) was
5 weighed in an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. After the attachment of a
nitrogen bleed, THF (20.0 mL) and diethyl chlorophos-
phite (2.00 mL) were added. After 17 hours the
10 polymerization was terminated via the addition of water,
THF and ether. The separated organic phase was again
washed with water. The organic phase was concentrated
at reduced pressure and then dried under vacuum
affording 4.73 g of polymer. GPC analysis (PS STD.):
15 Mn = 12200, Mw = 22600, PD = 1.85.

EXAMPLE 5Polymerization of THF withDiethyl Chlorophosphite and Dysprosium Triflate

In a dry box, dysprosium triflate (2.00 g) was
20 weighed in an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. After the attachment of a
nitrogen bleed, THF (20.0 mL) and diethyl chlorophos-
phite (2.00 mL) were added. After 17 hours the
25 polymerization was terminated via the addition of water,
THF and ether. The separated organic phase was again
washed with water. The organic phase was concentrated
at reduced pressure and then dried under vacuum
affording 9.80 g of polymer. GPC analysis (PS STD.):
30 Mn = 14100, Mw = 27900, PD = 1.98.

EXAMPLE 6Polymerization of THF withDiethyl Chlorophosphite and Tin Triflate

In a dry box, tin triflate (2.00 g) was weighed in
35 an oven dried 100 mL RB flask equipped with a stirring

bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphite (2.00 mL) were added. After 17 hours the polymerization was terminated via the addition of water, THF and ether. The separated organic phase was again washed with water. The organic phase was concentrated at reduced pressure and then dried under vacuum affording 14.93 g of polymer. GPC analysis (PS STD.): Mn = 2680, Mw = 5520, PD = 2.06.

EXAMPLE 7

Polymerization of THF with Diethyl Chlorophosphite and Bismuth Triflate

In a dry box, bismuth triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphite (2.00 mL) were added. After 17 hours the polymerization was terminated via the addition of water, THF and ether. The separated organic phase was again washed with water. The organic phase was concentrated at reduced pressure and then dried under vacuum affording 7.99 g of polymer. GPC analysis (PS STD.): Mn = 3050, Mw = 6600, PD = 2.16.

EXAMPLE 8

Polymerization of THF with Diethyl Chlorophosphite and Lanthanum Triflate

In a dry box, lanthanum triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphite (2.00 mL) were added. After 15 hours the polymerization was terminated via the addition of water,

THF and ether. The separated organic phase was again washed with water. The organic phase was concentrated at reduced pressure and then dried under vacuum affording 7.03 g of polymer. GPC analysis (PS STD.):

5 Mn = 14500, Mw = 30300, PD = 2.08.

EXAMPLE 10

Polymerization of THF with

Phosphonitrilic Trimer and Ytterbium Triflate

10 In a dry box, ytterbium triflate (2.00 g) and phosphonitrilic trimer (1.00 g) were weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) was added. After 16 hours the

15 polymerization was terminated via the addition of water, THF and ether. The separated organic phase was again washed with water. The organic phase was concentrated at reduced pressure and then dried under vacuum affording 7.78 g of polymer. GPC analysis (PS STD.):

20 Mn = 6710, Mw = 28500, PD = 4.25.

EXAMPLE 11

Polymerization of THF with

Vinyl Acetate and Ytterbium Triflate

25 In a dry box, ytterbium triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and vinyl acetate (1.00 mL) were added. After 17 hours the polymerization

30 was terminated via the addition of water, THF and ether. The resulting organic phase was separated, washed with water, concentrated at reduced pressure and then dried under vacuum affording 7.66 g of polymer. GPC analysis (PS STD.): Mn = 184000, Mw = 335000, PD = 1.82.

EXAMPLE 12Polymerization of THF with
Vinyl 2-Ethylhexanoate and Ytterbium Triflate

In a dry box, ytterbium triflate (2.00 g) was added
5 to each of four 100 mL RB flasks equipped with stirring
bars. The flasks were sealed with rubber septa and
removed from the dry box. After the attachment of
nitrogen bleeds THF (20.0 mL) was added to each flask.
10 Vinyl 2-ethylhexanoate (1.0, 2.0, 3.0 and 4.0 mL) was
added to each flask. After 17 hours the polymerizations
were terminated via the addition of water, THF and
ether. The separated organic phases were again washed
with water, separated, concentrated at reduced pressure
and then dried under vacuum. Polymer yields and GPC
15 analyses:

Vinyl 2-Ethyl- hexanoate (mL)	Polymer Yield (g)	Mn (PS STD.)	Mw	PD
1.0	1.47	435000	774000	1.78
2.0	1.85	429000	681000	1.59
3.0	2.28	410000	622000	1.52
4.0	3.07	253000	543000	2.15

EXAMPLE 13Polymerization of THF with Vinyl Acetate
and Bis(n-cyclopentadienyl)tetrahydrofuran-
bis(trifluoromethanesulfonato)zirconium
20 (Cp₂Zr[(O₃SCF₃)₂](THF))

In a dry box, bis(n-cyclopentadienyl)tetrahydro-
furan-bis(trifluoromethanesulfonato)zirconium
(Cp₂Zr[(O₃SCF₃)₂](THF)) (2.00 g) was weighed in an oven
dried 100 mL RB flask equipped with a stirring bar. The
25 flask was sealed with a rubber septum and removed from
the dry box. After the attachment of a nitrogen bleed,
THF (20.0 mL) and vinyl acetate (2.00 mL) were added.
After 17 hours the polymerization was terminated via the

addition of water, THF and ether. The resulting organic phase was separated, washed with water, concentrated at reduced pressure and then dried under vacuum affording 12.17 g of polymer. GPC analysis (PS STD.): Mn = 60100, Mw = 126000, PD = 2.10.

EXAMPLE 14

Polymerization of THF with Vinyl Acetate and Yttrium Triflate

In a dry box, yttrium triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and vinyl acetate (3.00 mL) were added. After 19.5 hours the polymerization was terminated via the addition of water, THF and ether. The resulting organic phase was separated, washed with water, concentrated at reduced pressure and then dried under vacuum affording 3.15 g of polymer. GPC analysis (PS STD.): Mn = 100000, Mw = 194000, PD = 1.94.

EXAMPLE 15

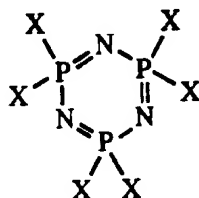
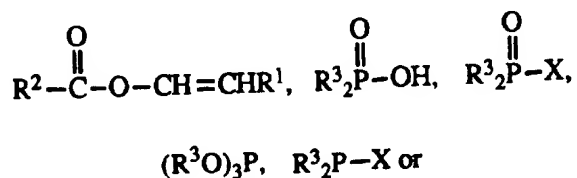
Polymerization of THF with Vinyl Acetate and Erbium Triflate

In a dry box, erbium triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and vinyl acetate (3.00 mL) were added. After 17 hours the polymerization was terminated via the addition of water, THF and ether. The resulting organic phase was separated, washed with water, concentrated at reduced pressure and then dried under vacuum affording 0.54 g of polymer. GPC analysis (PS STD.): Mn = 222000, Mw = 396000, PD = 1.76.

Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous
5 modifications, substitutions and rearrangements without departing from the spirit or essential attributes of the invention. Reference should be made to the appended claims, rather than the foregoing specification, as indicating the scope of the invention.

WHAT IS CLAIMED IS:

1. A process for the polymerization of cyclic ethers, comprising, contacting one or more oxiranes, oxetanes, tetrahydrofurans, oxepanes, 1,3-dioxolanes or
 5 1,3,5-trioxanes with a compound of the formula $MZ_3 \cdot Q_t$, and an accelerator which is a compound of the formula



wherein:

- R^1 is hydrogen, hydrocarbyl or substituted hydrocarbyl;
 10 R^2 is hydrogen, hydrocarbyl or substituted hydrocarbyl;
 each R^3 is independently hydrocarbyl or substituted hydrocarbyl;
 each X is independently chlorine, bromine or iodine;
 15 M is a metal selected from the group consisting of strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, cobalt, vanadium, niobium, tungsten, ruthenium,
 20 osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, aluminum, gallium, indium, thulium, germanium, tin, lead, arsenic, antimony and bismuth;
 at least one of Z is an anion of the formula $^{-}SO_3R^5$,
 25 wherein R^5 is perfluoroalkyl containing 1 to 12

carbon atoms or part of a fluorinated polymer wherein the carbon atoms alpha and beta to the sulfonate group are together bonded to at least four fluorine atoms, or tetraphenylborate, and the remainder of Z is oxo or one or more monovalent anions;

s is 1 when M is silver;

s is 2 when M is strontium, barium, cobalt, rhodium, iridium, palladium, platinum, chromium, zinc, cadmium or mercury;

s is 3 when M is scandium, yttrium, a rare earth metal, arsenic, antimony, bismuth, gold, iron, ruthenium, osmium, aluminum, gallium, indium or thulium;

s is 4 when M is titanium, zirconium, hafnium, molybdenum, germanium, tin, or lead;

s is 5 when M is rhenium, vanadium, niobium or tantalum;

s is 6 when M is tungsten;

Q is a neutral ligand;

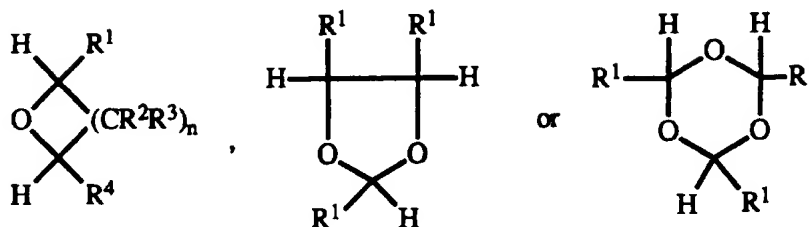
t is 0 or an integer of 1 to 6;

and provided that each oxo group present as part of Z is considered to account for two of s.

2. The process as recited in Claim 1 wherein said cyclic ether is one or more of said tetrahydrofurans, oxepanes, 1,3-dioxolanes or 1,3,5-trioxanes.

3. The process as recited in Claim 2 wherein M is a metal selected from the group consisting of strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, germanium, tin, lead, arsenic, antimony and bismuth.

4. The process as recited in Claim 3 wherein said cyclic ether comprises the formula



wherein:

each R^1 , R^2 , R^3 and R^4 is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms; and n is 2 or 4.

5. The process as recited in Claim 4 wherein n is 2 and R^1 , R^4 and all of R^2 and R^3 are hydrogen.

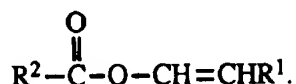
6. The process as recited in Claim 4 wherein n is 2 and R^1 and R^4 are each hydrogen, one of R^2 is hydrogen, the other R^2 is methyl, and both R^3 are hydrogen.

7. The process as recited in Claim 3 wherein R^5 is trifluoromethyl or perfluoroalkyl.

8. The process as recited in Claim 5 wherein M is strontium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, rhenium, iron, ruthenium, palladium, copper, gold, zinc, tin, bismuth or mischmetall.

9. The process as recited in Claim 1 carried out at a temperature of about -80°C to about 130°C .

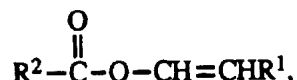
10. The process as recited in Claim 1 wherein said accelerator is a compound of the formula



11. The process as recited in Claim 10 wherein R^1 is hydrogen or alkyl, and R^2 is alkyl, phenyl, or substituted phenyl.

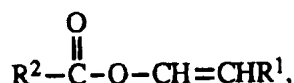
12. The process as recited in Claim 10 wherein R^1 is hydrogen and R^2 is methyl.

13. The process as recited in Claim 5 wherein said accelerator is



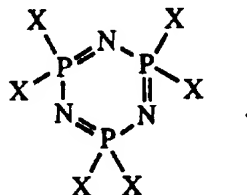
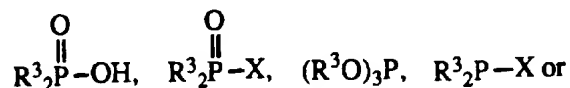
5 and R^1 is hydrogen or alkyl, and R^2 is alkyl, phenyl, or substituted phenyl.

14. The process as recited in Claim 5 wherein said accelerator is



and R^1 is hydrogen and R^2 is methyl.

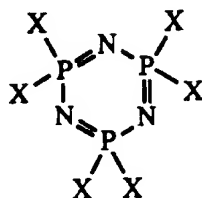
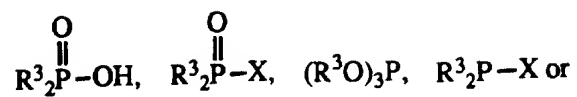
10 15. The process as recited in Claim 1 wherein said accelerator is



16. The process as recited in Claim 15 wherein each R^3 is independently alkyl, phenyl, or substituted phenyl, and X is chlorine.

15 17. The process as recited in Claim 15 wherein each R^3 is n-alkyl containing 1, 2, 3 or 4 carbon atoms or phenyl.

18. The process as recited in Claim 5 wherein said accelerator is



and each R^3 is independently alkyl, phenyl, or substituted phenyl, and X is chlorine.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/13701

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G65/10 C08G65/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,94 09055 (E.I. DU NEMOURS AND CO.) 28 April 1994 see claim 1 see page 7, line 22 ---	1-18
A	US,A,5 130 470 (SURIYANARAYAN D. ET AL) 14 July 1992 see claim 1 ---	1-14
A	FR,A,2 235 950 (MINNESOTA MINING AND MANUFACTURING CO.) 31 January 1975 see claim 1 ---	1-14
A	US,A,2 950 306 (SMITH W. C.) 23 August 1960 see claim 1; examples 4,5 ---	1,15-18
	--- -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

18 January 1996

Date of mailing of the international search report

16.02.96

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

O'Sullivan, T

INTERNATIONAL SEARCH REPORT

Int. Patent Application No.
PCT/US 95/13701

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 251 104 (ASHLAND OIL INC.) 7 January 1988 see claim 1; table 1 -----	1,15-18

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No
PCT/US 95/13701

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9409055	28-04-94	EP-A- 0665859	09-08-95
US-A-5130470	14-07-92	NONE	
FR-A-2235950	31-01-75	US-A- 3907706	23-09-75
		AU-B- 475892	09-09-76
		AU-B- 7088274	08-01-76
		CA-A- 1035491	25-07-78
		CH-A- 606195	31-10-78
		DE-A- 2432414	30-01-75
		GB-A- 1477363	22-06-77
		JP-C- 927259	13-10-78
		JP-A- 50038690	10-04-75
		JP-B- 53007151	15-03-78
US-A-2950306	23-08-60	NONE	
EP-A-0251104	07-01-88	US-A- 4683281	28-07-87
		JP-A- 63010619	18-01-88